PATENT ABSTRACTS OF JAPAN

(11)Publication number : 08-179123
(43)Date of publication of application : 12.07.1996

(51)Int.Cl. G02B 5/26
G02B 5/28

(21)Application number : 06-322967
(22)Date of filing : 26.12.1994

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(54) HARD-COAT FILM

(57)Abstract:
PURPOSE: To obtain a hard-coat film having a high refractive index, excellent in wear resistance and capable of being cured by cross-linking in a short time by forming the film with a composition contg. a specified component.
CONSTITUTION: The composition contg. a component A as a multifunctional acrylate and a component B as ≥1 kind of inorg. oxide fine grain selected from among antimony oxide, tin oxide, indium-tin mixed oxide, cerium oxide, titania and zirconia, is cured to constitute the hard-coat film. An acrylate having ≥2 functional groups in one molecule can be used as the multifunctional acrylate of the component A. The functional group curable with photopolymerization, an active energy beam such as electron beam and radiation and heat are used, and especially the photopolymerizable functional group is preferably used. Although the inorg. oxide fine grain used in the component B can be dispersed in the coating film on condition that the transparency of the film is maintained, a sol wherein the grains are dispersed in the form of colloid is most preferably used from the standpoint of operability, etc.

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[Date of sending the examiner's decision of rejection]

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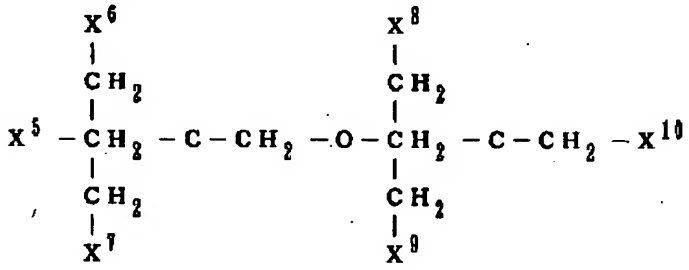
CLAIMS

[Claim(s)]
[Claim 1] Rebound ace court film characterized by consisting of a hardened material of the constituent containing following A component and B component.
A. It is [claim 2] more than a kind of the inorganic oxide particle chosen from polyfunctional acrylate B. antimony oxide, tin oxide, an indium tin mixed oxide, cerium oxide, a titania, and a zirconia. Rebound ace court film according to claim 1 with which this polyfunctional acrylate is characterized by having a photopolymerization nature functional group.
[Claim 3] Rebound ace court film according to claim 1 characterized by the refractive indexes of this hardened material being 1.53 or more and 1.68 or less.
[Claim 4] Rebound ace court film according to claim 3 characterized by including this inorganic oxide five to 50% of the weight.
[Claim 5] Rebound ace court film according to claim 1 characterized by the refractive indexes of this hardened material being 1.68 or more and 1.80 or less.
[Claim 6] Rebound ace court film according to claim 5 characterized by including this inorganic oxide 50 to 80% of the weight.
[Claim 7] Rebound ace court film according to claim 1 characterized by this polyfunctional acrylate being the monomer shown by the formula (I).
[Formula 1]



(At least three in a formula and of X5, X6, X7, X8, X9, and X10 pieces are a CH2 =CH-COO-radical, and the remainder is a -OH-radical.)

[Translation done.]

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DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Industrial Application] This invention relates to the rebound ace court film excellent in a high refractive index and abrasion resistance, transparency, chemical resistance, etc. It is suitably applied as the sheet plastic of which transparency is required, plastic film, etc., for example, is widely used for front covers, such as a cathode-ray tube (CRT), a flat display, and a covering case, an optical lens, the lens for glasses, window shielding, light covering, a helmet shield, etc.
[0002]
[Description of the Prior Art] As compared with glassware, it is lightweight, and it excels in shock resistance, and also a plastic part is cheap, it has the various advantages that fabrication is easy, and is widely used for various front panels, an optical related application, etc. However, since such moldings articles had the inadequate abrasion resistance of the front face, it had the fault by damage on the front face.
[0003] In order to cancel these faults, many proposals, such as a thermosetting bridge formation coating article or a photopolymerization system coating article, are made conventionally. For example, in JP,62-89902,A, an organic silane compound, polyfunctional epoxy, and the thermosetting bridge formation coating article it is unrefined from an antimony oxide particle are proposed. However, when abrasion resistance was satisfied, the refractive index seldom improved, and the completion of hardening took much time amount.
[0004] Moreover, about the thermosetting goods which have a high refractive index, the resin for high refractive-index lenses which consists of a polymer obtained by carrying out vinyl polymerization of the urethane-ized (meta) acrylic monomer which made the acrylic monomer which has a halogenation ring (meta), and polyfunctional isocyanate react to JP,2-12489,B is proposed. This approach had inadequate abrasion resistance, although the high refractive index was obtained.
[0005] On the other hand, according to JP,62-169833,A, the photo-curing monomer which consists of polyacrylate of dipentaerythritol is proposed about the photopolymerization nature bridge formation coating article, for example. Although the coating of the high degree of hardness [approach / this] in a short time is obtained, a refractive index is 1.55 or less and is unsuitable to the optical supply

which an interference fringe arises when it covers to a substrate with high refractive indexes, such as a polycarbonate, polyester carbonate or polyethylene terephthalate, Pori 1, and 4-cyclohexane dimethylene terephthalate, and requires high resolution.

[0006]

[Problem(s) to be Solved by the Invention] As above, in the conventional technique, there is no constituent which has a high refractive index and abrasion resistance, and carries out bridge formation hardening for a short time, and it aims at canceling the fault of this conventional technique in the invention in this application. Namely, this invention is a high refractive index, and it excels in abrasion resistance, and aims at offering further the rebound ace court film in which bridge formation hardening is possible for a short time.

[0007]

[Means for Solving the Problem] This invention has the following configuration, in order to attain the above-mentioned purpose.

[0008] "Rebound ace court film characterized by consisting of a hardened material of the constituent containing following A component and B component.

[0009] A. More than a kind of the inorganic oxide particle chosen from polyfunctional acrylate B. antimony oxide, tin oxide, an indium tin mixed oxide, cerium oxide, a titania, and a zirconia"

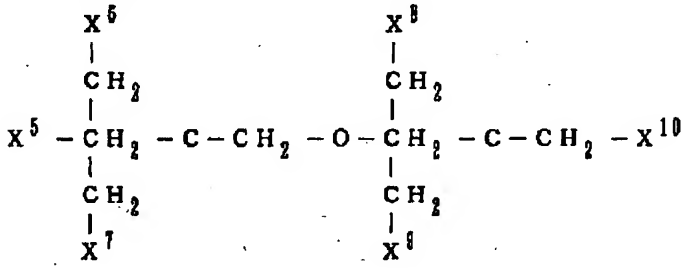
Although it can use if the polyfunctional acrylate of A component used by this invention is acrylate which has two or more functional groups in a monad, as this functional group, activity energy-line hardenability, such as photopolymerization nature, an electron ray, and a radiation, and a thermosetting thing are used, and a photopolymerization nature functional group is preferably used from a point with cheap equipment [fitness and equipment] hardening effectiveness etc. especially. As a photopolymerization nature functional group, although polymerization nature functional groups of partial saturation, such as an acryloyloxy radical, a methacryloyloxy radical, a vinyl group, a styryl radical, and an allyl group, etc. are raised, an acryloyloxy radical is suitably used especially in respect of being hard to receive transparency and oxygen inhibition in the ease of dealing with it etc. The thing of metaphor **** is used as concrete acrylate.

[0010] Neopentyl glycol acrylate, 1,6-hexanediol diacrylate, The acrylic-acid diester of alkylene glycol, such as propylene glycol diacrylate Triethylene glycol diacrylate, dipropylene glycol diacrylate, The acrylic-acid diester of polyoxy alkylene glycol, such as polyethylene-glycol diacrylate and polypropylene-glycol diacrylate The acrylic-acid diester of polyhydric alcohol, such as pentaerythritol diacrylate The acrylic-acid diester of ethylene oxide, such as 2-2'screw {4-(acryloxy diethoxy) phenyl} pro van and 2-2'screw {4-(acryloxy poly propoxy) phenyl} propane, and a propylene oxide addition product can be raised. Furthermore, it can blend with arbitration after taking into consideration the solubility of coating liquid, the transparency of a coat, etc. also about epoxy acrylate, urethane acrylate, and polyester acrylate. Rather than the above-mentioned polyfunctional bitter taste lied, more, in order to consider as the monomer excellent in the balance of a refractive index and a degree of hardness, the monomer which has three or more acryloyloxy is suitably used into 1 molecule

hung up below. Specifically, trimethylolpropane triacrylate, trimethylol triacrylate, PENTA glycero RUTORI acrylate, a (**) pentaerythritol thoria chestnut rate, (**) pentaerythritol tetraacrylate, dipentaerythritol pentaacrylate, dipentaerythritol hexaacrylate, TONOPENTA erythritol thoria KURIRETO, tripentaerythritol TETORATORI acrylate, tripentaerythritol HEKISATORI acrylate, etc. are raised. Especially, especially the polymerization activity of optical bridge formation in air is excellent in the (**) pentaerythritol thoria chestnut rate to which that from which three or more of the hydroxyl group of polyhydric alcohol are acrylic ester has three or more alcoholic hydroxyl groups in 1 molecule which is used more preferably and shown especially by the following general formula (I), (**) pentaerythritol tetraacrylate, dipentaerythritol pentaacrylate, especially dipentaerythritol hexaacrylate, etc., and they can obtain enough hardening coats.

[0011]

[Formula 2]



(At least three in a formula and of X5, X6, X7, X8, X9, and X10 pieces are a CH2 =CH-COO-radical, and the remainder is a -OH-radical.)

As an A component of this invention, it is the purpose of adjustment to raise the refractive index other than said indispensable component more etc., and the high refractive-index monofunctional acrylate which has the benzene ring is made [using suitably or]. As these monomers and a typical thing of oligomer, halogen nuclear substitution objects, such as these 1 chlorine, such as phenoxy ethyl acrylate, phenoxy polyethylene-glycol acrylate, 2-hydroxy-3-phenoxypropylacrylate, a 2-acryloyloxyethyl-2-hydroxyethyl phthalic acid, and 2-acryloyloxyethyl phthalic acid, and a bromine, etc. can be illustrated.

[0012] As a condition contained in the paint film of the inorganic oxide particle used of B component in this invention, the sol which distributed transparency from the point of workability and transparency grant to colloid as a desirable example especially although it was not limited especially when it was that of a disadvantage trap potato is raised in the state of a paint film. It is ** for which one or more sorts chosen from antimony oxide, tin oxide, an indium tin mixed oxide, cerium oxide, a titania, and a zirconia are specifically used. Furthermore, the sol of polar solvents, such as an alcoholic sol, dimethyl formamide, dimethylacetamide, and a cellosolve sol, can be suitably used rather than the hydrosol from soluble viewpoints, such as compatibility with A component, dispersibility, and a photoinitiator, a sensitizer. As a desirable sol, the sol of antimony oxide, tin oxide, and a titania can be raised especially.

[0013] As an inorganic oxide particle, although the thing of mean-particle-diameter

1-200mmicro is used suitably, the thing of the particle diameter of 5-100mmicro is used still more preferably. That to which mean particle diameter exceeds 200mmicro tends to reduce the transparency of a generation coat, and has the inclination for thick-film-ization to become difficult. Moreover, it is also desirable to add various kinds of surfactants and amines for improving the dispersibility of a particle. Furthermore, a problem does not have using together and using two or more sorts of inorganic oxide particles in any way, either.

[0014] Although especially the rate of a compounding ratio of A component and B component in this invention is not limited, it can be suitably chosen in the range which does not spoil transparency. Moreover, it is desirable to take the compounding ratio of B component into consideration towards making small a difference with the refractive index of a base material, and it is desirable to make the difference less than into 0.03. For example, when a base material is a polycarbonate, as for the rate of a compounding ratio of an inorganic oxide, it is desirable that it is 5 - 50 % of the weight among a coat, and, as for the refractive index of a paint film, it is desirable that it is 1.53 or more and 1.68 or less. At less than 5 % of the weight, when a refractive index and a degree of hardness have a small improvement effect and exceed 50 % of the weight, there is an inclination for an optical property to fall.

[0015] Moreover, in order to obtain the spreading film of reliance quantity refraction for the purpose of an antireflection film, as for the rate of a compounding ratio of an inorganic oxide, it is desirable that it is 50 - 80 % of the weight, and it is desirable that it is 1.68 or more and 1.80 or less as the refractive index. When the optical thickness in this application wavelength lambda applies the thin film of the integral multiple of 1/4lambda, it can form suitably. At less than 50 % of the weight, if the acid-resisting effectiveness is low and exceeds 80 % of the weight, the homogeneity of a coat will fall and adhesion will worsen.

[0016] In this invention, acetophenones, benzophenones, ketals, anthraquinone, thioxan tons, an azo compound, peroxides, 2, 3-dialkyl dione compounds, disulfide compounds, thiuram compounds, a fluoro amine compound, etc. are used as a polymerization initiator. The following are raised as an example of a photopolymerization initiator.

[0017] 2, a 2'-diethoxy acetophenone, p-dimethyl acetophenone, 1-hydroxy cyclohexyl phenyl ketone, 1-hydroxy dimethyl phenyl ketone, 2-methyl-4'-methylthio-2-MORIHORINO propiophenone, 2-benzyl-2-dimethylamino -1 -(4-MORIHORINO phenyl)- Acetophenones, such as butanone 1 Benzoin methyl ether, benzoin ethyl ether, benzoin iso-propyl ether, Benzoins, such as benzyl dimethyl RETARU, a benzophenone, 2, a 4'-dichloro benzophenone, There are benzophenones, such as 4, a 4'-dichloro benzophenone, and p-chlorobenzo phenon, 2 and 4, 6-trimethyl benzoyl diphenylphosphine oxide, anthraquinone, and thioxan tons. These photopolymerization initiators may be used independently, and two or more sorts may be combined or they may be eutectic mixture. The amount of the photopolymerization initiator used has desirable 0.2 - 10 weight section to the polymerization nature monomer constituent 100 weight section. As the light source required for said photopolymerization, the various mercury lamps and chemical lamp of low voltage, high pressure, and extra-high voltage, a metal halide

lamp, etc. are usable. Since exposure effectiveness is good especially, a high-pressure mercury lamp is used suitably.
[0018] A constituent is heated if needed, composition of an urethane-ized acrylic monomer is promoted or the constituent in this invention can also remove content low volatile matter. Moreover, it can heat after photopolymerization and can also perform considering heat curing suitably from advancing hardening more.
[0019] Since a uniform solution condition is made, an organic solvent can be blended with the constituent in this invention in the range which does not spoil the purpose of this invention for the purpose of improvement in the spreading engine performance etc. As an organic solvent, that whose boiling point is about 60-150 degrees C can use suitably on the spreading engine performance. As a concrete example, aromatic series solvents, such as acetic-ester system solvents, such as ether-alcohols, such as alcohols, such as isopropyl alcohol, n-propyl alcohol, and isobutyl alcohol, methyl cellosolve, butyl cellosolve, and methyl carbitol, ethyl acetate, and butyl acetate, toluene, and a xylene, etc. are raised. Even when these are independent, they are used, and two or more sorts can be mixed and they can also be blended.
[0020] In the constituent of this invention, polymerization inhibitor, a leveling agent, a thickener, a coloring inhibitor, an ultraviolet ray absorbent, a silane coupling agent, an antistatic agent, an adhesion grant agent, etc. may be added if needed. After adjusting solution concentration suitably and applying to a predetermined substrate, mainly although the constituent in this invention carries out optical bridge formation, it can apply suitably the methods of application usually performed, such as immersion coating, knife coating, spray coating, flow coating, a spin coat, a call coat, a curtain coat, a slit-die coat, and a KURABIA coat, as a spreading means.
[0021] As goods which apply this invention rebound ace court film, a transparence substrate is desirable. If transparent, even if it is a glass substrate and a plastic plate, it will be used without being limited especially.
[0022] Instantiation of a transparence substrate raises glass, polymethylmethacrylate and its copolymer, jetty RECHIN glycol bisallyl carbonate ("CR-39"), a polycarbonate, polyester KABONETO, polyethylene terephthalate, Pori 1, 4-cyclohexane dimethylene terephthalate, polystyrene, styrene / maleic resin, styrene/acrylonitrile copolymer, poly chloro styrene, a polyvinylidene chloride, polyether SARUFOFUN, a polyarylate (U polymer) sheet, etc. The polycarbonate whose refractive index is 1.55 or more especially, polyester carbonate, polyethylene tele FUTARE, Pori 1, 4-cyclohexane dimethylene terephthalate, polystyrene, styrene / maleic resin, styrene/acrylonitrile copolymer, a poly chloro styrene polyvinylidene chloride, a polyether ape phon, polyarylate (U polymer), etc. are most preferably used for this invention.
[0023] Since it excels in a high refractive index and abrasion resistance, transparency, chemical resistance, etc., the goods which covered the rebound ace court of this invention are suitably used as the sheet plastic of which transparency is required, plastic film, etc., and can be especially used as an optical material. Furthermore, a cathode-ray tube, a flat display (used also as the front plates or these equipment components for an input of various displays, such as a laser

display, a photochromic display, electrochromic display, a liquid crystal display, a plasma display, a light emitting diode display, and electro luminescent BANERU.) In addition, it is widely used for front covers, such as a covering case, an optical lens, the lens for glasses, window C RUTORI, light covering, a helmet shield, etc. Moreover, when using as an optical material, as for the coating article of a high refractive index, it is also desirable to prepare the covering hardened material of a low refractive index in a surface from the point of acid resisting.

[0024] Hereafter, although the example of this invention is raised, this invention is not limited to these examples.

[0025]

[Example]

The 1-hydroxy cyclohexyl phenyl ketone 1 weight section and the 2-methyl-4'-methylthio-2-MORIHORINO propiophenone 2 weight section were added as the pentaerythritol thoria chestnut rate 70 weight section and a photopolymerization initiator as an example 1A component, and it stirred and dissolved. Subsequently, the antimony oxide 30 weight section (30% methanol sol solution) was blended. the silicone system surface-active-agent 0.5 weight section -- subsequently the butyl-acetate 20 weight section was added, and coating liquid was prepared.

[0026] (2) The coating liquid in which the coating article carried out creation preparation was applied to the polycarbonate substrate of 1.0mm thickness in dip coating, and it was left for 2 minutes, subsequently dried for 5 minutes at 70 degrees C, and the solvent was removed. They are 2000 mj/cm2 with high pressure mercury vapor lamp 2 LGT of 1kw in an air ambient atmosphere. It irradiated and optical bridge formation was performed.

[0027] (3) The evaluation coating article of a coating article was evaluated according to the following item and the approach. The result was indicated to Table 1.

[0028] (b) Thickness of a coating article It measured with the surface roughness plan (SE-330 Kosaka Laboratory make).

[0029] (b) The 100 squares of bonding strength spacing of 1mm were prepared, and it judged with the exfoliation number of the squares in 90-degree exfoliation with a Scotch tape.

[0030] (c) Refractive index It measured by the phase contrast measuring method (ellipsometry).

[0031] (d) Abrasion-proof nature Visual observation of the existence of the crack of the front face was carried out for the film front face after 20 round-trip abrasion with the rubber (LION NO50) under 1kg load. The valuation basis was carried out as follows.

[0032] O; -- **: which a crack does not attach at all -- x: which a crack attaches a little -- (e) interference fringe in which many cracks take lessons or a paint film exfoliates The visual judgment was performed by reflection of a twin fluorescent lamp, and it judged by the size of an interference fringe.

[0033] The coating article was obtained like the example 1 except having changed the point made into the phenoxy ethyl acrylate 30 weight section as the pentaerythritol thoria chestnut rate 40 weight section and a B component as an example 2A component. The evaluation result was shown in Table 1.

[0034] as an example 3A component -- as the pentaerythritol thoria chestnut rate 30 weight section and B component -- as the tin oxide 70 weight section (30% phosphorus dope tin oxide benzyl alcohol sol) and a photopolymerization initiator -- 2-methyl-4' -- the coating article was obtained like the example 1 except having changed the point which carried out - methylthio-2-MORIHORINO propiophenone 1.5 weight section addition. The evaluation result was shown in Table 1.
[0035] If the point using the ITO70 weight section (30% tin oxide dope ITO benzyl alcohol sol) as an example 4B component was removed, the coating article was obtained like the example 3. The evaluation result was shown in Table 1.
[0036] On the rebound ace court film obtained in the example 5 example 1, the same coat as an example 3 was prepared by the optical thickness of 1/2lambda. Adhesion was good. Furthermore, 2% ("SAITOPPU", Asahi Glass Co., Ltd. make) liquid of amorphous fluororesins of a low refractive-index perfluoro polyether was applied to the surface by one fourth of optical thickness. A surface reflection factor (the one side reflection factor with a wavelength of 550nm was measured with the spectrophotometer using the specular reflection fixture of 12 degrees of incident angles) is 0.5%, and it checked having a good acid-resisting function.
[0037] B component of example of comparison 1 example 1 was not added, and also the coating article was obtained by the same approach as an example 1. The evaluation result was indicated to Table 1.
[0038] A component was not added in example of comparison 2 example 3, and also the coating article was obtained by the same approach as an example 3. The evaluation result was indicated to Table 1.
[0039]
[Effect of the Invention] The rebound ace court film of this invention has the following effectiveness.
[0040] (1) A refractive index is high and excellent in an antifriction property.
[0041] (2) When a refractive index applies to a comparable substrate, a reflective interference fringe does not arise but it is used suitable for an optical application.
[0042] (3) By photo-curing, a bridge can be constructed in a short time and excel in productivity.

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